# Synthesis of Hyperbranched Polyisobutylenes by Inimer-Type Living Polymerization. 1. Investigation of the Effect of Reaction Conditions

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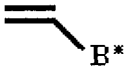
*Received August 21, 2000; Revised Manuscript Received November 14, 2000*

ABSTRACT: Hyperbranched polyisobutylenes (PIBs) have been synthesized by carbocationic copolymerization of an *inimer* (*ini*tiator-mono*mer*, *IM*) and isobutylene (IB). The *IM* used was 4-(2-methoxyisopropyl)styrene (*p*-methoxycumylstyrene, pMeOCumSt), in conjunction with $TiCl_4$ as a co-initiator in methylcyclohexane (MeCHx)/methyl chloride (MeCl) 60/40 v/v solvent mixture at −80 °C, in the presence of 2,6-di-*tert*-butylpyridine (D*t*BP) as a proton trap. The effect of reaction conditions on the molecular weights (MW), molecular weight distributions (MWD), and branching frequencies (BR) was investigated. Hyperbranched PIBs with MWs up to $M_n \approx 8 \times 10^5$ g mol$^{-1}$ and MWD as low as 1.2 were obtained within 15−60 min reaction time, where under the same conditions the 2-chloro-2,4,4-trimethylpentane (TMPCl) monofunctional initiator would have yielded MWs in the range of $M_n \approx 10^4$ g/mol. BRs were determined by selective destruction of the branching points (links) and taking the ratio of the MWs before and after link destruction. The experimental BR values, ranging from 3 to 57, agreed reasonably well with values calculated using the formula $BR = (M_n/M_{n(theo)}) - 1$, where $M_n$ is the total MW of the hyperbranched PIB, and $M_{n(theo)}$ would be the MW if the *IM* would act as initiator only. The process was scaled up to 400 g of PIB/batch, sufficient for meaningful physical characterization.

## Introduction

During the past decade, with the success and improvement of living ionic polymerizations, a surge of enthusiasm has appeared on branched polymers.[1−3] Branched polymers are of substantial commercial interest, due to markedly lower viscosity and less shear sensitivity then their linear counterparts.[3] Among all the existing branched polymers, dendrimers appear to be the most interesting because of their spherical symmetry.[4−6] They can be prepared by divergent or convergent methods, applying strictly controlled protection−condensation−deprotection sequences.[7] *Dendrimers* have a controlled and symmetric structure and very narrow molecular weight distribution (MWD). However, the often complicated and time-consuming synthetic routes associated with this class of branched polymers present a major drawback in commercial application. Flory[8] discussed an easier alternative route that relies on a "one-pot polycondensation" of $AB_n$ monomers, yielding so-called *hyperbranched* polymers. These polymers are less symmetric than dendrimers and have lower branching frequencies (BR) and most probable MWDs. While the "one-pot polycondensation" is simple compared to dendrimer synthesis, the reaction times are often very long (10−100 h).

A novel approach was introduced in the early 1990s by Fréchet et al.,[4,9,10] termed "self-condensing vinyl polymerization" (SCVP), allowing the synthesis of hyperbranched structures using vinyl monomers carrying an initiating group, B*, as shown below:




As such species combine features of a monomer and an initiator, later they were called "*inimer*" (*IM*).[11,12] This synthetic strategy is a cascade reaction initiated by the reaction of the active B* site with a vinyl group (A) of another *IM*, forming a dimer which now possesses two active sites, A* and B*, and a vinyl group A. Both the active A* and B* can now react with a vinyl group of either another *IM* or a dimer, etc., finally leading to hyperbranched structures which will possess a number of end groups and active centers. The kinetics of this type of polymerization resemble polycondensation, and often very long reaction times are necessary to obtain high molecular weight (MW) hyperbranched polymers.

Gauthier et al.[13] introduced *arborescent* polymers. These combine the characteristics of *dendrimers* and *hyperbranched* polymers.[7] Arborescent polymers are prepared by successive grafting of polymeric building blocks (graft-on-graft) and have well-defined structure and narrow MWD but relatively low BRs. High-MW arborescent polystyrenes and polyisoprenes were prepared successfully by this method, but the synthetic method is rather laborious and lengthy.[7,13,14]

A novel alternative, commercially feasible route for the synthesis of *hyperbranched* polymers was introduced recently.[11] In this approach a small amount of suitable *IM* is copolymerized with an olefin. High-MW hyperbranched PIB was successfully synthesized by this method using 4-(2-hydroxyisopropyl)styrene) as *IM* in a "one-pot" living-type polymerization system by Puskas et al.[12] The synthetic strategy is shown in Figure 1. $M_n$ = 355 000 g/mol was reached in 60 min reaction time. The multimodality of the MWD of this PIB indicated that living PIB chain ends can react with another polymer with unreacted vinyl functionality (essentially a "macromonomer"). Interestingly, the proposed hyperbranched structure shown in Figure 1 was first reported by Nuyken et al.[15] in an attempt to polymerize PIB macromonomers.

Müller et al.[16] simulated a copolymerization system similar to that shown in Figure 1, assuming equality of all rate constants. According to their model, the system

10.1021/ma001467x CCC: $20.00 
Published on Web 01/12/2001

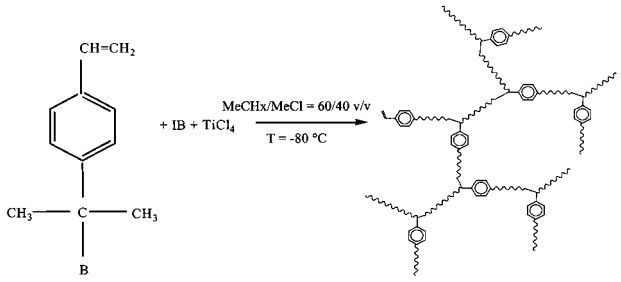



**Figure 1.** Synthetic strategy for the preparation of hyperbranched PIBs.

would resemble a living polymerization at low conversion, while at high conversion self-condensing vinyl polymerization (SCVP) would occur. MW, MWD, and BR were predicted to depend strongly on the *IM*/M ratio. Preliminary experimental data for the group transfer SCVP of the *IM* 2-(2-methyl-1-triethylsiloxy-1-propenyloxy)ethyl methacrylate with methyl methacrylate showed the predicted trends for MWs, but the experimental values were substantially lower than predicted and the *IM*/M ratio did not show an effect on MWD.

The present paper describes initial investigations into the effect of reaction conditions on the structure of hyperbranched PIBs prepared using 4-(2-methoxyisopropyl)styrene (*p*-methoxycumylstyrene, pMeOCumSt) as an *IM*, preliminary characterization of the polymers, and the successful synthesis of high-MW hyperbranched PIBs on a relatively large scale (400 g/batch).

## Experimental Section

**Materials.** Methylcyclohexane (MeCHx) (Aldrich) was distilled from calcium hydride prior to use. Methyl chloride (MeCl) and isobutylene (IB) (Matheson) were dried by passing the gaseous materials through in-line gas purifier columns packed with $CaCl_2$/BaO. They were condensed in the cold bath of the polymerization glovebox prior to use. 2,6-Di-*tert*-butylpyridine (D*t*BP) (Aldrich) was used as received. Degassed methanol was used to quench the reactions. Neutral aluminum oxide (Aldrich, Brockman activity 1) was partially deactivated with water (about 20 mL of water for 300 g of aluminum oxide).

4-(2-Methoxyisopropyl)styrene (*p*-methoxycumyl styrene, pMeOCumSt) was synthesized as follows:

To a 500 mL round-bottom flask, equipped with a reflux cooler, containing 50 mL of THF, freshly distilled from calcium hydride, and 12 g of dry magnesium turnings, was added dropwise a solution of 25 g (0.136 mol) of distilled *p*-bromostyrene in 100 mL of dry THF. The formation of the Grignard reagent was initiated by the addition of few iodine crystals. After completion of the addition (about 4 h), an excess of dry acetone (30 mL, 0.399 mol) was added dropwise. The reaction mixture was left under nitrogen overnight, and then an excess of methyl iodide (100 mL, 1.56 mol) was added dropwise. To avoid any homopolymerization, the temperature of the reaction flask was kept below 30 °C. After 6 h reaction time, the mixture was poured into 1 L of saturated aqueous $NH_4Cl$ solution and extracted twice with diethyl ether. The combined organic phases were washed with distilled water, dried over $MgSO_4$, and filtered, and the solvents were evaporated. The amount of crude product recovered was 18.4 g (76.8% yield). The crude product was added to 200 mL of reagent grade pentane and purified by flash column chromatography over neutral aluminum oxide, partially deactivated with water. The pentane was removed with a rotavap at room temperature to give 14.4 g (0.082 mol, 60.3% yield) of pure product. The $^1$H and $^{13}$C NMR peak assignments and spectra of the purified pMeOCumSt (a new compound by CAS registry search) are shown in Table 1 and in the "Supporting Information" (Figures S1 and S2).

**Table 1. Assignment of the $^1$H and $^{13}$C NMR Spectra of pMeOCumSt**

| H | $\delta_H$ (ppm) | C | $\delta_C$ (ppm) |
|---|---|---|---|
| 1 | 3.37 | 1 | 51.5 |
| 3, 4 | 1.18 | 2 | 80.8 |
| 6, 10 | 7.45 | 3, 4 | 27.7 |
| 7, 9 | 7.44 | 5 | 146.8 |
| 11 | 6.71 | 6, 10 | 126.8 |
| 12a | 5.12 | 7, 9 | 127.8 |
| 12b | 5.78 | 8 | 135.7 |
| | | 11 | 136.7 |
| | | 12 | 114.4 |

**Procedures. a. Polymerizations**. Polymerizations were carried out under a dry nitrogen atmosphere ($H_2O$, <1 ppm; $O_2$, <5 ppm) in an MBraun LabMaster 130 glovebox at −80 °C. The moisture and oxygen contents were monitored continuously. The hexane bath was cooled by liquid nitrogen quickly, and the temperature was maintained at −80 °C with an FTS Flexi Cool immersion cooler. A 500 mL three-neck round-bottom flask, equipped with an overhead stirrer, was charged with the cosolvents (MeCHx/MeCl, 60/40 v/v) and other reactants. The addition sequence of the reactants was as follows: CumOMeSt, D*t*BP, and IB. The total reaction volume was 250 mL. The reaction was started by the rapid addition of a chilled stock solution of $TiCl_4$ in MeCHx. Specific concentrations are given in the text and figure captions. The reactions were quenched after completion as indicated by real-time IR monitoring, by addition of prechilled methanol. MeCl was evaporated, and the polymer was dissolved in Hx. The solution was washed with distilled water, dried over $MgSO_4$, filtered, and precipitated into a large excess of methanol and dried in a vacuum oven for 1 week.

Large-scale polymerizations were conducted using the same procedure, replacing the 500 mL three-neck round-bottom flask by 5−12 L three-neck round-bottom flasks.

**b. IR Monitoring**. The polymerization reactions were monitored in situ using an attenuated total reflectance (ATR) fiber-optic mid-IR probe (Remspec Inc.). Semilogarithmic first-order monomer consumption plots were obtained by the ratio of the 1656 $cm^{-1}$ peak area at any given time relative to the area at time = 0, i.e., prior to the addition of $TiCl_4$. A detailed description of this novel real-time monitoring method has been given.[17−19]

**c. Polymer Characterization**. Polymer $M_n$s, $\bar{M}_w$s, and MWDs were determined by size exclusion chromatography (SEC) using a Waters system equipped with six Styragel-HR columns ($10^6$, $10^5$, $10^4$, $10^3$, 500, and 100 Å pore sizes), thermostated at 35 °C, a Waters 410 DRI detector thermostated at 40 °C, a Dawn DSP 18 angle laser light scattering detector (MALLS) (Wyatt Technology), and a Waters 996 PDA detector. The mobile phase was THF at 1 mL/min, continuously distilled off $CaH_2$, and recirculated. MWs were calculated by using the universal calibration principle (UCP) which was shown to be valid for linear PIBs.[20] Absolute MWs were obtained by using the Astra software (Wyatt Technology). Since their *IM* content was less than 1%, the hyperbranched PIBs were assumed to be pure PIB, so $dn/dc = 0.093$ given for PIB[21] was used for the calculations. This method gave good agreement with values calculated assuming 100% mass recovery.

$^1$H and $^{13}$C NMRs were conducted using a Varian Gemini 300 MHz NMR in $CDCl_3$ as solvent.

**d. Link Destruction**. Kennedy et al. reported the selective destruction of the aromatic core in a three-arm star-branched PIB.[22] This was adapted for the hyperbranched PIBs as follows: To a solution of 1% PIB in 75 mL of $CCl_4$ was added under agitation 36 mL of a solution of aqueous 30% $H_2O_2$ in trifluoroacetic acid. Samples were taken at regular intervals and characterized by SEC. The reactions were allowed to proceed for 72 h, and the final products were analyzed by SEC.

## Results and Discussion

**Effect of Reaction Conditions.** In branched polymers, the branching frequency or degree of branching

**Table 2. Effect of the $[IM]_0/[M]_0$ Ratio in the *Inimer* Polymerization of IB. $[IB]_0$ = 2.0 mol/L; $[DtBP]$ = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; $T$ = −80 °C**

| sample ID | $[TiCl_4]_0$, mol/L | $[IM]_0$, mol/L | $[IM]_0/[M]_0$ | MALLS[a] $\bar{M}_n$, $10^3$ g/mol | MALLS[a] $\bar{M}_w$, $10^3$ g/mol | UCP[b] MWD | UCP[b] $\bar{M}_n$, $10^3$ g/mol | $\bar{M}_{n,theor}$, $10^3$ g/mol | BR[c] theor | BR[c] exp |
|---|---|---|---|---|---|---|---|---|---|---|
| 3 | 0.02 | 0.002 | 0.001 | 97 | 130 | 1.4 | 110 | 56.1 | 0.3 | 7 |
| 2 | 0.04 | 0.004 | 0.002 | 88 | 158 | 1.8 | | 28.0 | 2.1 | |
| 6 | 0.06 | 0.006 | 0.003 | 38 | 75 | 2.0 | 45 | 18.7 | 1.0 | 3 |
| 7 | 0.08 | 0.008 | 0.004 | 77 | 223 | 3.4 | 80 | 14.0 | 4.5 | 4.6 |
| 5 | 0.1 | 0.01 | 0.005 | 88 | 236 | 2.7 | 195 | 11.2 | 6.9 | 8.9 |
| 4 | 0.2 | 0.02 | 0.01 | 100 | 217 | 2.2 | 112 | 5.6 | 0.8 | 4.1 |

[a] Absolute molecular weight by multiangle laser light scattering. [b] Universal calibration principle. [c] BR = branching frequency ($M_n/M_{n,theor}$) − 1.

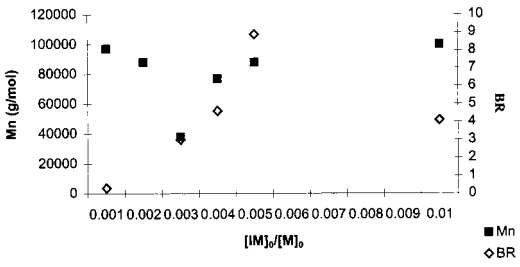



**Figure 2.** Dependence of $\bar{M}_n$ and BR on $[IM]_0/[M]_0$ ratios in *inimer* IB polymerizations. $[IB]_0$ = 2.00 mol/L; $[TiCl_4]_0$ = 10$[IM]_0$; $[DtBP]$ = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; $T$ = −80 °C (data in Table 2).

**Table 3. Effect of the $[TiCl_4]_0$ Concentration on the *Inimer* Polymerization of IB. $[IB]_0$ = 2.0 mol/L; $[IM]_0$ = 0.008 mol/L; $[DtBP]$ = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; $T$ = −80 °C**

| sample ID | $[TiCl_4]_0$, mol/L | MALLS[a] $\bar{M}_n$, $10^3$ g/mol | MALLS[a] $\bar{M}_w$, $10^3$ g/mol | UCP[b] MWD | UCP[b] $\bar{M}_n$, $10^3$ g/mol | BR[c] theor | BR[c] exp |
|---|---|---|---|---|---|---|---|
| 8 | 0.016 | 110 | 230 | 2.1 | 104 | 6.9 | 9.2 |
| 11 | 0.048 | 71 | 151 | 2.1 | 78 | 4.1 | 5.4 |
| 10 | 0.064 | 68 | 144 | 2.1 | 70 | 3.9 | 6.7 |
| 7 | 0.08 | 77 | 223 | 2.9 | 205 | 4.5 | 4.6 |
| 12 | 0.096 | 43 | 76 | 1.8 | 50 | 2.1 | 3.5 |

[a] Absolute molecular weight by multiangle laser light scattering. [b] Universal calibration principle. [c] BR = branching frequency, ($\bar{M}_n/\bar{M}_{n,theor}$) − 1; $\bar{M}_{n,theor}$ = 14 × $10^3$g/mol.

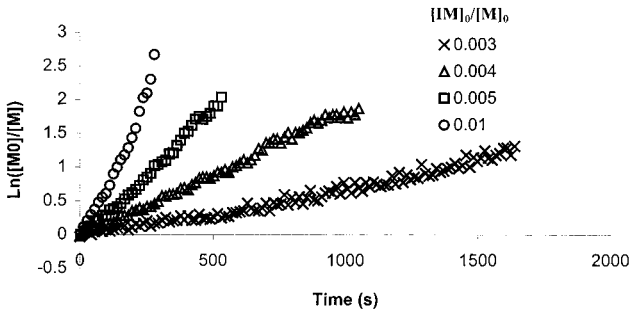



**Figure 3.** Semilogarithmic rate plots of *inimer* IB polymerizations by IR monitoring. $[TiCl_4]_0$ = 10$[IM]_0$, $[IB]_0$ = 2.0 mol/L; $[DtBP]$ = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; $T$ = −80 °C (data in Table 2).

(BR) is one of the most important parameters. In an *inimer*-type copolymerization of IB (see Figure 1), in addition to the relative concentration of the $[IM]/[M]$, the degree of branching will be influenced by other parameters as well. Recently, we have reported investigation of the kinetics of living IB polymerization, initiated by the 2-chloro-2,4,4-trimethylpentane/titanium tetrachloride (TMPCl)/$TiCl_4$) initiator/co-initiator system in methylcyclohexane (MeCHx)/methyl chloride

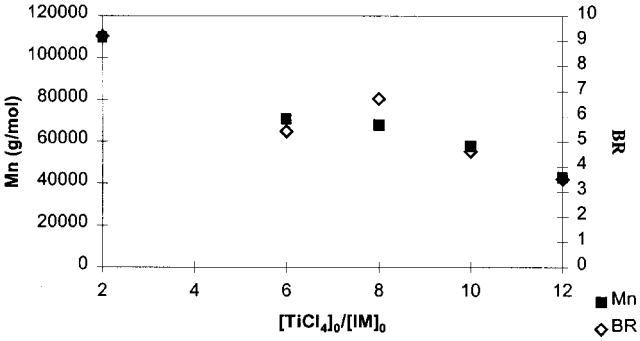



**Figure 4.** Dependence of $\bar{M}_n$ on $[TiCl_4]_0/[IM]_0$ ratios in *inimer* IB polymerizations. $[IM]_0$ = 0.008 mol/L, $[IB]_0$ = 2.0 mol/L; $[DtBP]$ = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; $T$ = −80 °C (data in Table 3).

(MeCl) or hexane (Hx)/MeCl 60/40 v/v at −80 °C, with a ratio of initiator to co-initiator higher than one.[19] Under these conditions, the reaction order in $TiCl_4$ was found to be close to 1. Monomer concentration and temperature were found to have a profound effect on the polymerization. $k_p'$, the apparent rate constant of polymerization ($k_p' = K_{eq}k_p$, where $K_{eq}$ is constant of the dormant−active chain equilibrium characteristic of living IB polymerization and $k_p$ is the polymerization rate constant), increased exponentially with an increase of $[IB]_0$ or a decrease in temperature. More surprisingly, the kinetics of the polymerization appeared to be very sensitive to solvent impurities. Indeed, the investigation revealed that $k_p'$ varied from 0.5 to 1.7 $L^2$ $mol^{-2}$ $s^{-1}$ and from 1.7 to 3.4 $L^2$ $mol^{-2}$ $s^{-1}$ in methylcyclohexane (MeCHx) and hexane (Hx), respectively, from two different providers and/or with and without further purification. The comprehensive kinetic/mechanistic scheme proposed for living IB polymerization[18] proposed two competitive reaction pathways. One is first order in $[TiCl_4]$ which dominates under $TiCl_4$ deficiency relative to $[I]_0$ as discussed above, while the other is second order in $[TiCl_4]$ and dominates when excess $TiCl_4$ relative to $[I]_0$ is used. Since both pathways proceed simultaneously, the experimental $[TiCl_4]$ reaction order was measured to be 1.76. This value agrees with others published in the literature.[23,24] The reaction order in [I] was found to be unity, in agreement with other researchers.[25−29] According to our present understanding,[19,30] the initiation step is greatly affected by the first-order pathway and very sensitive to solvent quality and $[IB]_0$ (i.e., polarity), while the overall propagation is dominated by the second-order pathway. Thus, in an *inimer*-type IB polymerization BR will most likely be influenced by the relative rates of initiation and propagation. With this understanding, we set out to investigate the effects of reaction conditions on the synthesis of hyperbranched PIBs.

**Table 4. Scale-up of *Inimer* IB Copolymerizations for the Preparation of 400 g/Batch Hyperbranched PIBs. $[IB]_0 = 2.0$ mol/L; $[IM]_0 = 0.004$ mol/L; $[TiCl_4]_0 = 0.08$ mol/L; [D*t*BP] = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; $T = -80$ °C**

| | | | MALLS[b] | | UCP[c] | | BR[d] | |
|---|---|---|---|---|---|---|---|---|
| sample ID | $\bar{M}_{n,theor}$ | $[M]_0 + [M]$,[a] mol/L | $\bar{M}_n$, g/mol | $\bar{M}_w$, g/mol | MWD | $\bar{M}_n$, $10^3$g/mol | theor | exp |
| 18[e] | 14 000 | 2 + 1 | 596 000 | 790 000 | 1.3 | 300 | 42 | 44.1 |
| 17 | 28 000 | 2 + 2 | 392 000 | 1 039 000 | 2.6 | 214 | 14 | 11.6 |
| 20 | 14 000 | 1 + 1 | 561 000 | 681 000 | 1.2 | 238 | 40 | 33.0 |
| 19 | 14 000 | 1 + 2 | 765 000 | 984 000 | 1.3 | 357 | 55 | 57.2 |

[a] Incremental monomer addition. [b] Absolute molecular weight by multiangle laser light scattering. [c] Universal calibration principle. [d] BR = branching frequency ($M_n/M_{n,theor}$) − 1. [e] $[IM]_0 = 0.008$ mol/L.

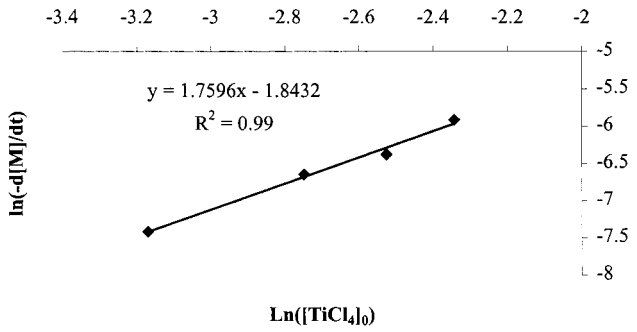



**Figure 5.** $\ln(-d[M]/dt)$ vs $\ln[TiCl_4]_0$ plot in *inimer* IB polymerizations. $[IB]_0 = 2.0$ mol/L; $[IM]_0 = 0.008$ mol/L; [D*t*BP] = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; $T = -80$ °C (data in Table 3).

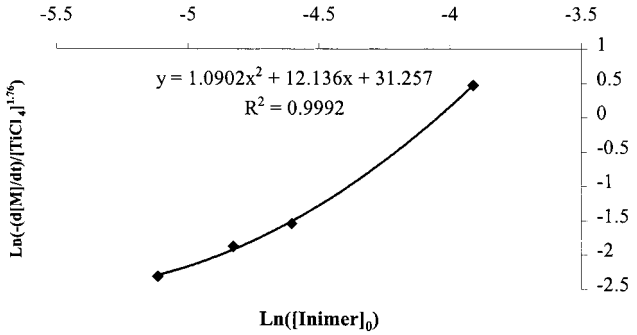



**Figure 6.** $\ln(-d[M]/dt)[TiCl_4]^{1.76}$ vs $\ln[IM]_0$ plot in *inimer* IB polymerizations. $[IB]_0 = 2.0$ mol/L; [D*t*BP] = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; $T = -80$ °C (data in Table 3).

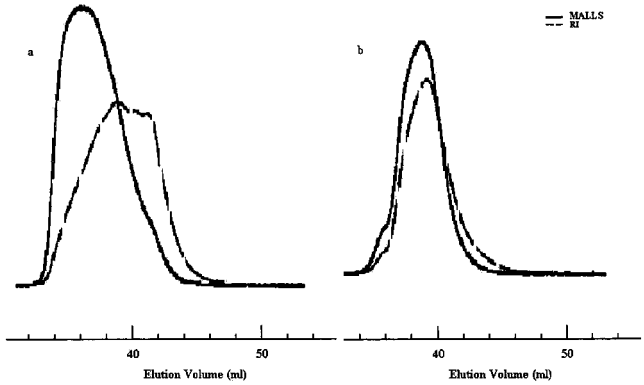



**Figure 7.** SEC traces of hyperbranched PIBs: (a) sample 17 and (b) sample 19 (data in Table 4).

**a. Effect of $[IM]_0/[M]_0$.** Table 2 shows the results of a series of experiments where the $[IM]_0/[M]_0$ was varied while $[M]_0$ and the $[TiCl_4]_0/[IM]_0$ ratio were kept constant at 2 mol/L and 10, respectively. The branching frequency can be defined as follows:

$$BR = [M_n/M_{n,theo}] - 1 \qquad (1)$$

where $M_{n,theo}$ would be the $M_n$ if all *IM* were acting as initiator only. Thus, if a polymerization were started with two *IM*s and one initiated and one copolymerized creating a linking site, BR would be 1. Table 2 lists the calculated BR values.

Figure 2 shows the dependence of $\bar{M}_n$ on $[IM]_0/[M]_0$. First the $\bar{M}_n$ decreases with $[IM]_0/[M]_0$ as expected when the *IM* mostly initiates, and then it increases as the $\bar{M}_n$ decrease is counterbalanced by branching before leveling off. The MWs measured by MALLS and UCP agree within experimental error, most likely due to the low BR values. It is known that UCP underestimates the MW of highly branched polymers[7] (see data in Table 3). Theoretical BR values (plotted in Figure 2) increase with increasing $[IM]_0/[M]_0$, before dropping at higher ($[IM]_0/[M]_0 = 0.01$) ratios. Figure 3 shows selected semilogarithmic rate plots obtained by real-time IR monitoring. The rate plots are linear for lower $[IM]_0/[M]_0$ ratios; for $[IM]_0/[M]_0 = 0.01$, however, it shows a slight curvature. Polymerization rate increased with increasing *IM* and $TiCl_4$ concentrations as expected, and a reasonably fast reaction was achieved at $[TiCl_4]_0 = 0.08$ mol/L. On the basis of the above trends, we selected $[M]_0 = 2$ mol/L, $[IM]_0/[M]_0 = 0.004$, and $[TiCl_4]_0 = 0.08$ mol/L for further investigations.

**b. Effect of $[TiCl_4]_0$.** Table 3 shows the results of a series of experiments conducted with a fixed $[IM]_0 = 0.008$ mol/L concentration ($[IM]_0/[M]_0 = 0.004$), while varying $[TiCl_4]_0$. Figure 4 shows the dependence of $\bar{M}_n$ and BR on the $[TiCl_4]_0/[IM]_0$ ratio. Both $\bar{M}_n$ and BR show a decreasing trend with increasing $[TiCl_4]_0/[M]_0$, while the MWD values do not display a clear trend (see Table 3). Again, MWs by UCP and MALLS agree within experimental error, reflecting on the low BR values. $[TiCl_4]_0$ order = 1.76 was found from the correlation between the ln of the polymerization rate ($\ln(-d[M]/dt)$ or $\ln k_{app}$, the slope of linear semilogarithmic plots obtained by *real-time* IR monitoring, similar to those shown in Figure 3) and $\ln[TiCl_4]_0$, as shown in Figure 5. The same reaction order was found in "regular" living IB polymerizations, while the rate of initiation was first order in $[TiCl_4]_0$.[18] The significance of this is that a decrease in $[TiCl_4]_0$ will cause a steeper drop in the overall rate of polymerization than that of the initiation step, a factor of great importance in recipe design. The reaction order in [*IM*] can be obtained by plotting $\ln(-d[M]/dt)$ or $k_{app}$ normalized by $[TiCl_4]_0^{1.76}$ to account for the varying $[TiCl_4]_0$ concentration; Figure 6 shows the trend obtained by IR monitoring. It is not linear as expected, since the *IM* serves both as an initiator and a monomer.

**c. Large-Scale Synthesis of High-MW Hyperbranched PIBs**. On the basis of the results of our investigations, we scaled up the preparation of hyperbranched PIBs to 400 g/batch for physical characterization. Table 4 shows conditions and results for these

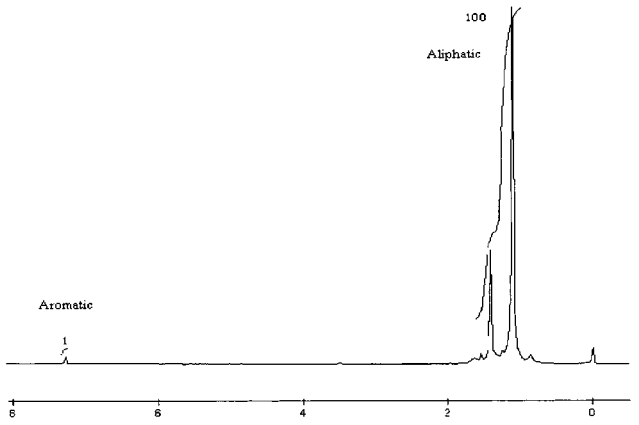



**Figure 8.** Proof of *inimer* incorporation NMR; $^1$H NMR spectrum of a hyperbranched PIB. $\bar{M}_n$ = 34 000 g/mol, $[IM]_0/[M]_0$ = 0.02.

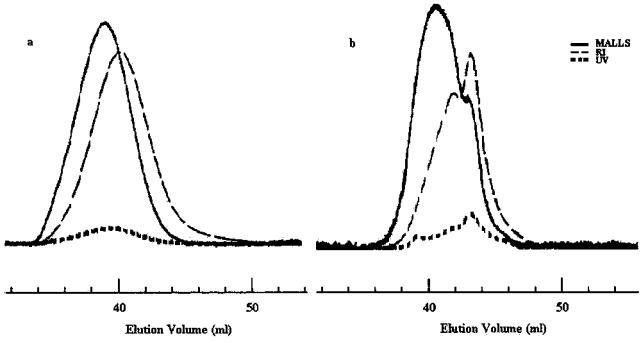



**Figure 9.** Proof of *inimer* incorporation by SEC, MALLS, RI, and UV traces of selected samples: (a) $\bar{M}_n$ = 139 000 g/mol; (b) $\bar{M}_n$ = 149 000 g/mol (multimodal MWD, chain−chain coupling).

experiments (samples 17−20). Very high MWs were achieved using incremental IB additions as specified. Selecting a $[TiCl_4]_0$ = 0.08 mol/L assured fast reactions (30−60 min total reaction time). Decreasing $[IM]_0$ by half decreased both MW and BR, since the $[TiCl_4]_0/[IM]_0$ ratio increased from 10 to 20 (see samples 18 and 17 in Table 4), which was found to have a depressing effect as shown in Figure 4. The broad MWD and multimodality of sample 17 (see Figure 7) indicates polymer−polymer coupling. Decreasing the $[IM]_0/[M]_0$ ratio to 0.004 by decreasing $[M]_0$ to 1 mol/L resulted in higher $M_n$'s and BRs (samples 19 and 20). The MWDs of samples 18−20 are quite narrow, with a very small shoulder on the high-MW side on the SEC trace (see sample 19 in Figure 7), which indicates very little coupling between polymer chains. The SEC traces of samples 17 and 19, shown in Figure 7, highlight the sensitivity of the MALLS signal toward high-MW species compared to the RI signal. As can be seen from Table 4, MW values for all samples by MALLS are considerably higher than by UCP, in accordance with high BR values. Mechanical and rheological characterizations of these polymers are in progress.

**Initial Characterization of Hyperbranched PIBs. a. IM Incorporation**. Because of the low [*IM*]/[M] ratios, IR monitoring did not allow us to follow the consumption of the inimer; thus, *IM* incorporation was verified by $^1$H NMR and SEC. A representative $^1$H NMR spectrum is shown in Figure 8. The [*IM*]/[M] ratio was calculated by comparing the aromatic and aliphatic regions and was found to be 0.02. The agreement with the feed ratio demonstrates 100% *IM* incorporation. SEC

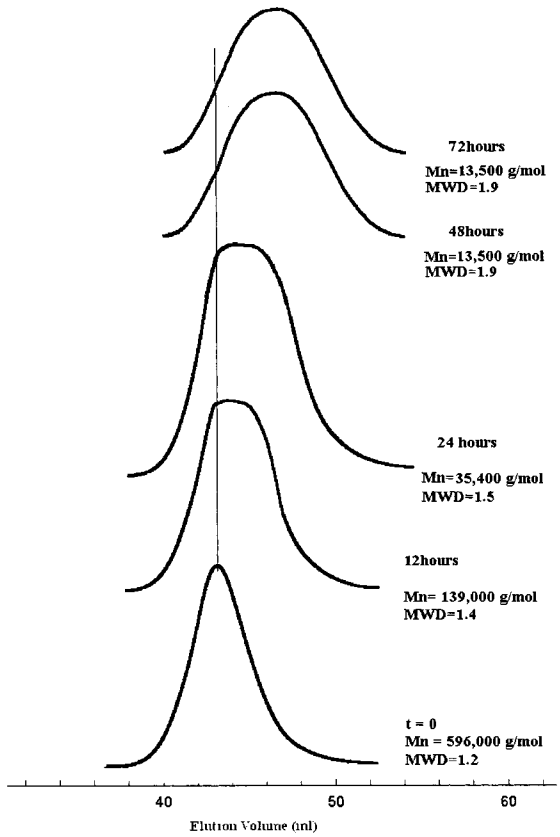



**Figure 10.** Selective destruction of a hyperbranched PIB (sample 18, data in Table 4).

characterization confirmed *IM* incorporation. Figure 9 displays SEC traces for selected samples. As PIB is transparent to UV so the UV trace demonstrates *IM* incorporation. The multimodality of sample *b* indicates chain−chain coupling, while the MWD in sample *a* is monomodal and narrow.

**b. Link Destruction.** The polymers were subjected to a link destruction procedure to get experimental information on the branching frequency. This is based on the "the core destruction method"[17] used to characterize star-branched PIBs. This method is said to selectively destroy the aromatic rings without affecting the PIB chains. Figure 10 shows SEC traces during a link destruction experiment together with the original SEC trace of sample 18, $\bar{M}_n$ = 596 000 g/mol. Complete destruction of the links occurred in 48 h as the MW of the polymer was reduced to $\bar{M}_n$ = 13 500 g/mol and remained constant after 72 h. Tables 2−4 list the experimental BR values, calculated using the formula $BR = (M_n/M_{n(theo)}) - 1$, where $M_n$ is the total MW of the hyperbranched PIB and $M_{n(theo)}$ would be the MW if the *IM* would act as initiator only, together with the calculated ones. The experimental BR values, ranging from 3 to 60, agree reasonably well with calculated values.

In conclusion, high molecular weight *hyperbranched* PIBs were synthesized by a convenient *inimer*-type polymerization. Reaction conditions were selected on the basis of the results of the investigation into the effect of reaction conditions on the structure of the polymers. Selective destruction of the branching points allowed the experimental determination of branching frequencies, which showed good agreement with calculated values. Characterization of the materials is in progress.

**Acknowledgment.** The authors thank the Bayer-NSERC (Natural Sciences and Engineering Research Council of Canada) Industrial Research Chair Program and NSERC for financial support.

**Supporting Information Available:** $^{1}H$ and $^{13}C$ NMR spectra of 4-(2-methoxyisopropyl)styrene (*p*-methoxycumylstyrene, pMeOCumSt). This material is available free of charge via the Internet at http://pubs.acs.org.

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MA001467X